ADVANCED POLYIMIDE BASED COMPOSITES FOR IMPROVED PROCESSING

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Abstract

A new matrix resin system, consisting of a commercially available cyanate ester, an oligomeric phenylethynyl terminated imide and a compatibilizer for both systems is used for the manufacturing of CFRP laminates by LCM processes. The solubility of the polyimide within the cyanate ester as well as the physio-chemical and mechanical properties of the unreinforced resin in the cured and uncured state are determined using various characterisation techniques. Based on these investigations, the optimum process conditions for the manufacturing of CFRP structures are determined. The thermal and mechanical properties of the CFRP laminates manufactured by handlaminating and VARTM are determined. The manufactured CFRP laminates show very good thermal and mechanical stability up to temperatures of 250°C over a longer period of time.

1. Introduction

Currently the applications of polymer based composites in aerospace parts exposed to higher temperatures (>250°C) are limited. Carbon fiber reinforced composites (CFRP) that are manufactured with commercially available epoxy resins have a minor long-term durability under elevated temperatures compared to other thermoset systems, such as cyanate esters, bismaleimides or polyimides. Especially polyimides show superior properties in terms of thermal stability, mechanical performance even under elevated temperatures and long term thermal stability compared to standard aerospace materials. However, these systems are relatively costly and present challenges during processing. In this regard, polyimides suffer from very high melt viscosities and very high curing temperatures, which restricts their commercial applications tremendously.

After the first synthesis of solvent based and so called *polymerized monomeric reactant* (PMR) polyimides by United States Airforce and NASA research programs[1], the development of polyimide resin systems have attracted a large interest in the field of high temperature resins. Due to the fact that PMR resins suffer from complex and lengthy cure cycles as well as extended postcures, microcracking is often a problem.[2] A promsising alternative to PMR resins are phenylethynyl terminated imides, so called PETI resins.[3] Unlike PMR resins, PETI resins are based on oligomeric phenylethynyl terminated imides, whereby the toxic diamine species is covalently bonded in the imide structure. This means that no toxic volatiles are emitted during the crosslinking of the uncured resins. A commonly used anhydride species for endcapping is phenylethynyl phthalic anhydride[4], which is mainly responsible for the high costs of the raw materials. PETI resins show good toughness, microcracking resistance and excellent thermooxidative stability in the cured state.[2] Nevertheless, PETI resins possess injection temperatures of 250°C to 300°C with viscosities of ~1000 mPas[5] and must be cured at 350°C to 400°C, which cannot be realised in any civil aerospace program. For that reason, suitable modification strategies have to be developed in order to make PETI resins processable in commercial processes.

Hamerton and Barton[6] showed that a copolymerisation of cyanate esters and bismaleimides is a promising solution for toughening of brittle cyanate esters without the loss of the thermal properties. As cyanate esters and bismaleimides do not react directly with each other, a chain extender in the form of an allylic bisphenol A compound is added to the resin mixture. It could be shown that an ene-reaction followed by a Diel-Alder reaction and stabilizing rearomatisation takes place during the

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crosslinking of these three compounds. In this regard, recent studies demonstrated that the commercially available compound diallyl bisphenol A (DABPA) is one of the most effective modifiers for BMI resins to improve the mechanical properties even under elevated temperatures.[7] In recent studies we could show that a coreaction between commercially available cyanate esters and PETI resins take place, when a suitable compatibilizer is added to the resin mixture.[8] In this regard, a proposed mechanism for the reaction between allylic pendant groups of the compatibilizer and the phenylethynyl functions of the PETI resin was described based on DSC, DMTA, TGA and SEM studies.[8] This coreaction resulted in a material that showed very unique properties in terms of thermal and mechanical performance. This study describes the manufacturing of CFRP structures by LCM techniques with the recently developed resin system. More precisely, the properties of the resin mixture for LCM approaches are investigated concerning an optimised process window. Furthermore, the mechanical properties of the CFRP structures with the resin mixture are determined.

2. Experimental

2.1. Materials and Methods

A commercially available novolac based cyanate ester **CE** (*Primaset PT 15*® from Lonza Group AG (CHE)) and a phenylethynyl terminated imide **PI** (*PETI 330*® from UBE Industries Ltd. (JPN)) in combination with 2,2´-diallylbisphenol A **DABPA** (GP Chemicals Inc. (USA)) are used for the formulation of the uncured resin mixtures. All chemicals are used without further purification steps. Before using, the **CE** is degassed at 80°C for 30 min. After the addition of **PI** and **DABPA**, the resulting mixture is degassed at 90°C for 45 min.

For the manufacturing of carbon fiber reinforced laminates, a G0939 fabric (Hexcel Corp. (USA)) was used as fiber reinforcement. Nine plies of G0939 with a setup of $[0]_{4S}$ are stacked to achieve a laminate thickness of ~2 mm. This setup is used in all manufacturing trials.

2.1.1. Preparation of CFRP laminates by handlaminating

After the resin is degassed at 90°C, the mixture is heated to 100°C and applied onto every ply of the setup so that a fibre volume content of approximately 55% is achieved. The entire setup is heated to 100°C and vacuum is applied (Figure 1). The composite laminate is cured with the following cure cycle:

1. 100°C → 150°C (2 K/min)
2. 150°C → 1 h isotherm
3. 150°C → 180°C (2 K/min)
4. 180°C → 2.5 h isotherm
5. Free standing postcure in convection oven: 250°C for 1 h and 300°C for 2.5 h

After the curing cycle a degree of cure of approximately 98% is achieved (determined by DSC).

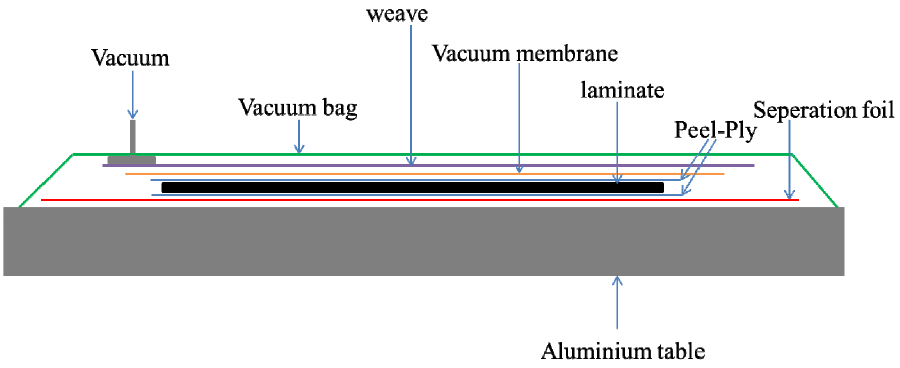

Figure 1: Setup for handlaminating process.

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2.1.2. Preparation of CFRP laminates by vacuum assisted resin transfer molding (VARTM)

The setup for VARTM approach is illustrated in Figure 2.

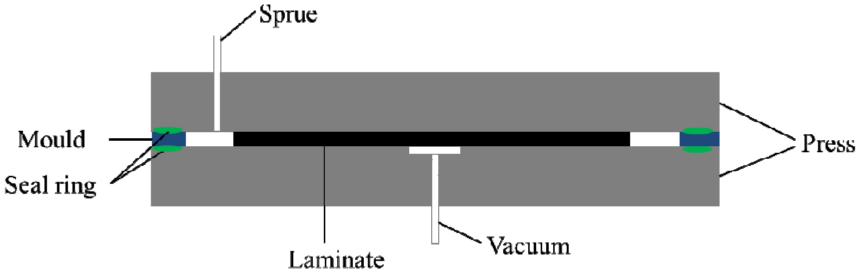


Figure 2: Setup of VARTM approach.

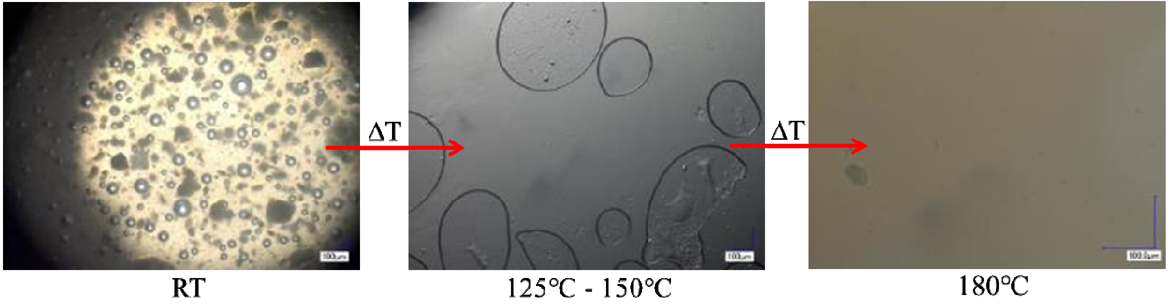
After the resin is degassed at 90°C, the mixture is heated to 130°C in a convection oven and is placed in a 130°C hot injection vessel. The dry G0939 fabric is placed in the press and the setup is heated to 150°C. A pressure of the press of 600 kN and vacuum is applied. Afterwards, the resin is infiltrated with a pressure of 1 to 3 bar into the G0939 fabric. When the setup is fully impregnated, the following cure cycle is applied:

1. 150°C → 180°C (2K/min)
2. 180°C → 2.5 h isotherm
3. Free standing postcure in convection oven: 250°C for 1 h and 300°C for 2.5 h.

After the curing cycle a degree of cure of approximately 98% is achieved (determined by DSC).

3. Results and Discussion

A major requirement for LCM processes is that the uncured resin system is a homogenous low viscous liquid. This means that the uncured resin matrix must be free of phase separated additives. The combination of a commercial PETI resin and a cyanate ester is based on the observation that the uncured **PI** shows a very good solubility within the **CE** at elevated temperatures, which is shown by the microscopy investigations illustrated in Figure 3.



RT 125°C - 150°C 180°C

Figure 3: Microscopy investigations of a mixture of **PI** (solid phase at RT) and **CE** (liquid phase at RT) at different temperatures.

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Figure 3 shows that a good solubility of **PI** in **CE** can be achieved at temperatures over 125°C. If such a resin combination would be cured with the help of a suitable catalyst for the cyanate ester or at elevated temperatures, a fully non-covalent interpenetrating polymer network (IPN) would result. In such a fully non-covalent IPN, the thermal and mechanical performance of the resulting material is restricted by the component with the lowest properties. In order to combine the favourable properties of **PI** (e.g. mechanical properties and long-term thermal stability) with the high desirable properties of **CE** (e.g. low viscosity, very low moisture uptake) and to reduce the negative properties of both resins, a suitable compatibilizer in terms of 2,2´-diallylbisphenol A **DABPA** must be added. **DABPA** is able to react with **CE** and **PI** so that the two separated networks are covalently connected with each other in the cured state. The coreactio of **DABPA** with **CE** and **PI** is described elsewhere[8].
Based on the DSC experiments presented in recent studies[8], suitable curing cycles are postulated, which are described in chapter 2.1.1. In addition, investigations of the unreinforced resin properties are performed depending on the amount of **PI** that is added to the resin mixture. The results are illustrated in Figure 4.

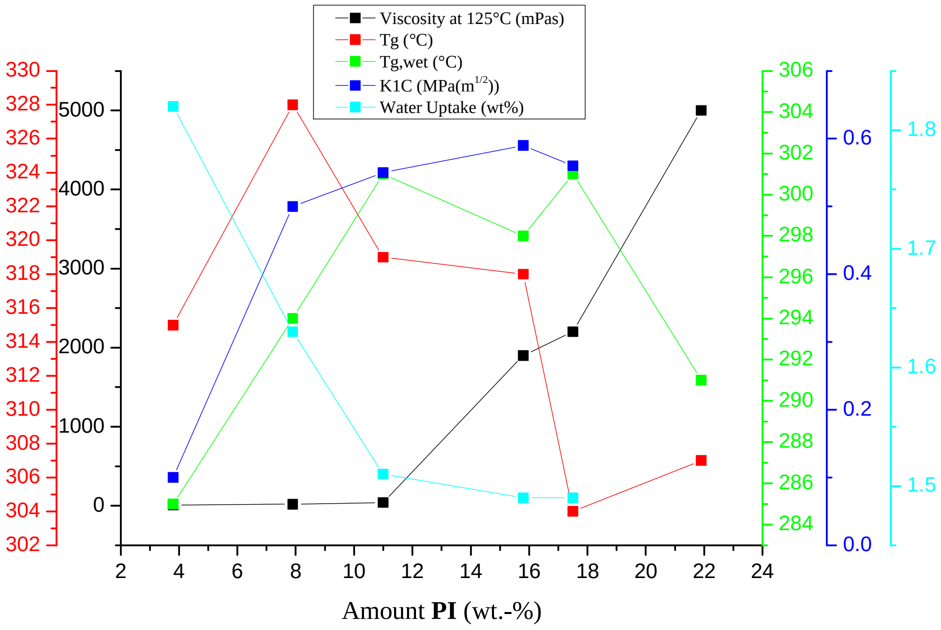

Figure 4: Summary of neat resin properties of a resin mixture of **CE/PI/DABPA**.

In Figure 4 one can see that the T_g in terms of the maximum of tan(δ) of the fully cured materials is between 304°C and 328°C. With an increasing amount of **PI**, the T_g first increases but decreases at amounts of **PI** greater than 8 wt.-%. This effect can be attributed to a decreased crosslink density of the thermoset network deriving from the mixture of two components. Furthermore, the K_{IC} value increases with an increasing amount of **PI** from 0.05 MPa√m up to 0.59 MPa√m. Moreover, the water uptake of the materials is measured by immersion of coupons in 70°C destilled water for 14 days. Figure 4 shows that the water uptake of the materials decreases with an increasing amount of **PI**. A constant water uptake of ~1.5 wt.-% is achieved at high amounts of **PI**. In the uncured state, it can be observed that the viscosity of the materials at 125°C increases with an increasing amount of **PI**. Up to an amount of 11 wt.-% **PI**, the viscosity is smaller than 500 mPas. This low melt viscosities and the results from the dissolution experiments show that the **CE/PI/DABPA** materials can be used in common LCM processes. On the basis of the results obtained from the characterisations of the neat resins in Figure 4, an optimum amount of 11 wt.-% of **PI**, 86.25 wt.-% **CE** and 2.75 wt.-% **DABPA** is chosen for further resin characterizations and for the manufacturing of all CFRP laminates. The properties of the unreinforced resin plate manufactured with such a composition is summarized in Table 1.

Table 1: Summary of the properties of **CE/PI/DABPA** unreinforced resin plate with a composition of 86.25 wt.-% **CE**, 11 wt.-% **PI** and 2.75 wt.-% **DABPA**.

T_g (°C)	$T_{g,wet}$ (°C)	T_{onset} (°C)	$T_{onset,wet}$ (°C)	$T_{5d,O2}$ (°C)	$\eta_{125°C}$ (mPas)	K_{IC} (MPa√m)	Water Uptake (wt.-%)
320	301	278	263	424	40	0.55	1.51

Additionally, the thermooxidative properties of the unreinforced resin mixture are investigated in comparison to commercial epoxy aerospace material for structural bearing parts and the unmodified *Primaset PT 15®* cyanate ester **CE** as reference. The results from the thermooxidative experiments are summarized in Figure 5.

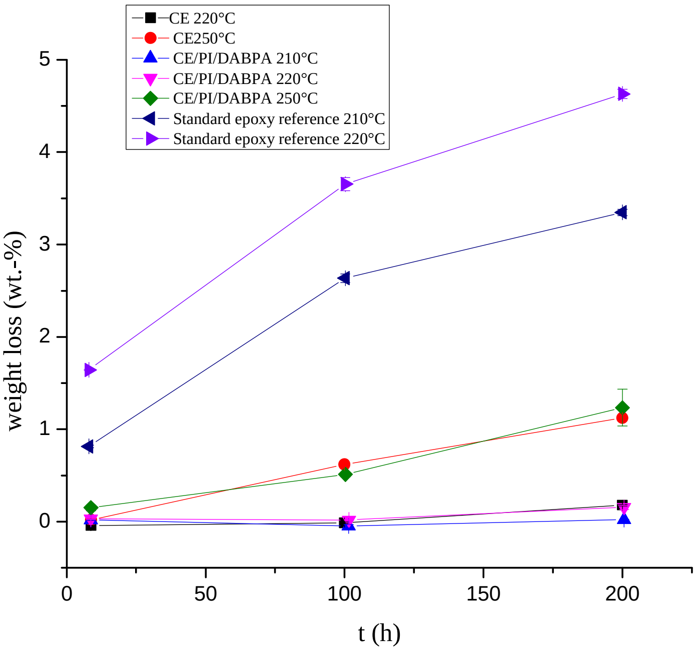

Figure 5: Summary of thermooxidative degradation experiments of **CE/PI/DABPA** with 11 wt.-% **PI** (blue, magenta, green), **CE** (black, red) and standard epoxy aerospace material (navy, violet) at temperatures of 210°C, 220°C and 250°C.

The thermooxidative degradation behavior of the **CE/PI/DABPA** material with 11 wt.-% **PI** is similar to the thermooxidative properties of the neat **CE** resin. Both thermosets show a very low weight loss at temperaturs above 220°C. No weight loss can be observed at 210°C and 220°C. At 250°C the weight loss is below 1.2 wt.-% after 200 h. In comparison to the high temperature resistant materials, the weight loss of the standard epoxy aerospace material is significantly higher at 210°C and 220°C, which means that the new matrix system shows superior thermal properties. In comparison to standard cyanate ester material, the new resin system shows at least the same thermooxidative properties but superior water uptake and significantly increased mechanical properties (see Figure 4).

Two approaches for the manufacturing of CFRP structures with the new thermoset system are considered. First, CFRP structures are manufactured using a simple handlaminating process. The setup for such a process is illustrated in Figure 1 (see chapter 2.2.2.). The process parameters as well as the cure cycle of the laminates are reported in chapter 2.2.2. as well. In order to obtain a good dissolution quality of the **PI** in the **CE**, an isotherm at 150°C is intercalated before curing at 180°C. After postucring at 300°C, the profile of the CFRP laminates obtained by handlaminating process showed a good optical quality, which was investigated by microscopy (Figure 6, upper left and right).

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Nevertheless, the developed thermoset matrix system should be applied in an industrial process that is reliable and reproducible. Hence, VARTM experiments with the new matrix resin system are performed. The setup of this process (Figure 2) as well as the process paramters are reported in chapter 2.2.2. After postucring, the profile of the CFRP laminate obtained by VARTM is illustrated in Figure 6 (bottom left and right). It shows that the laminates manufactured by VARTM have less ondulations and a better fiber volume fraction than the laminates obtained by handlaminating. Moreover, the VARTM laminates show to have a consistant thickness over the entire laminate.

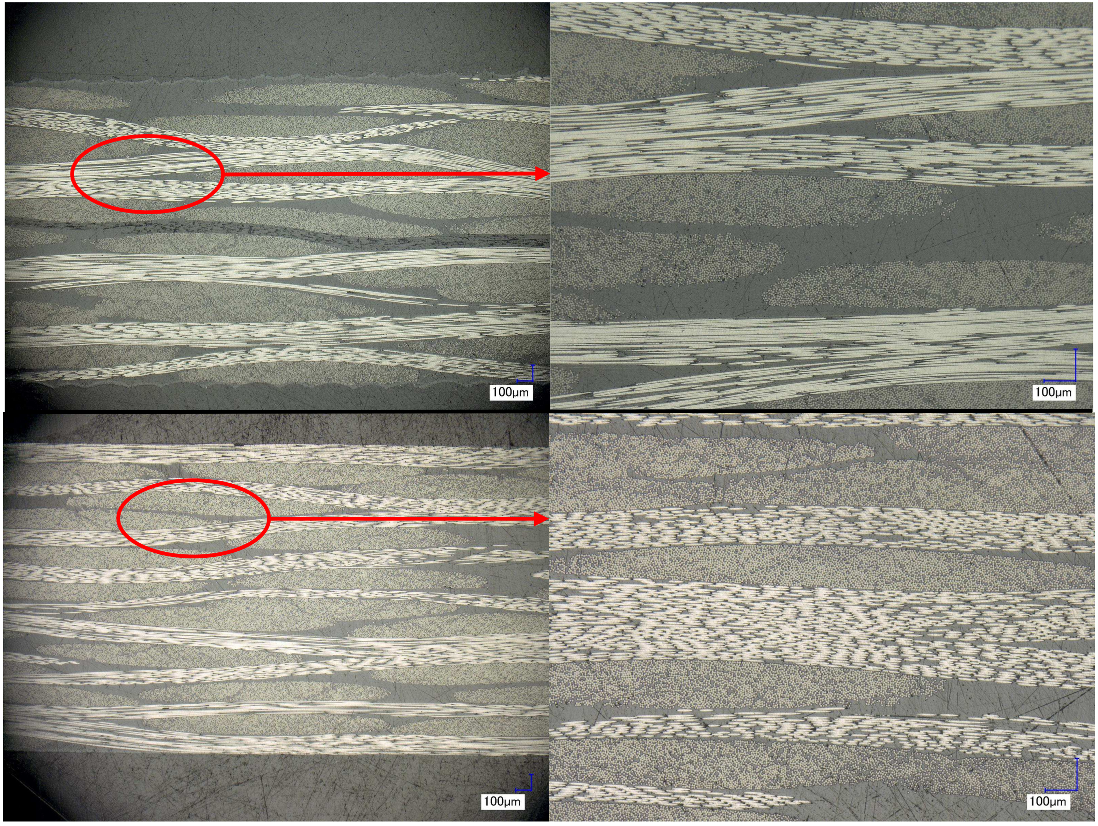

Figure 6: Microscopy pictures of the profiles of CFRP laminates with **CE**/**PI**/**DABPA** (11 wt.-% **PI**) resin matrix and G0939 fabirc: upper left and right: handlaminating; bottom left and right: VARTM.

The infiltration of the resin in the course of the VARTM process is performed at 130°C. The physical condition of the uncured **CE**/**PI**/**DABPA** mixture at 130°C is homogenous, low viscous liquid. Hence, no isothermal temperature step at 150°C must be performed to obtain a good solubility of **PI** in **CE**. In order to investigate the processability of the resin system and to guarantee suitable process window, rheological experiments are performed (Figure 7).

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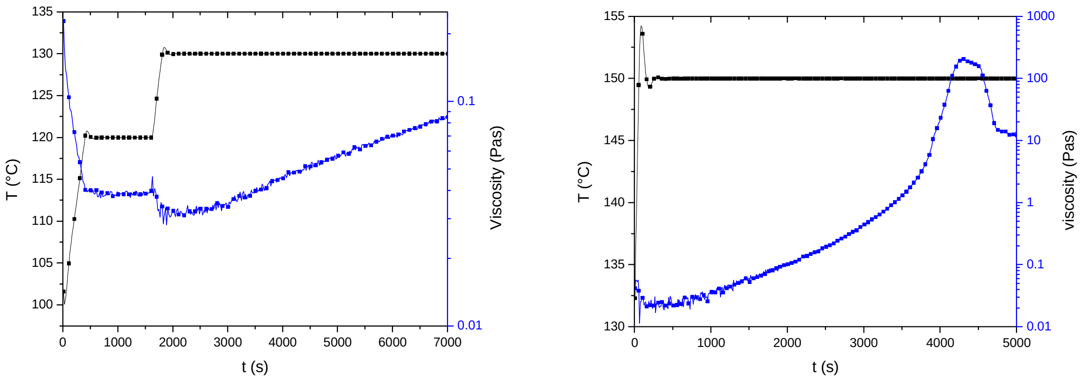

Figure 7: Isothermal viscosity measurements of **CE/PI/DABPA** with 11 wt.-% **PI**. Left: isothermal at 120°C and 130°C; right: isothermal at 150°C.

The left graph in Figure 7 illustrates that the resin system possesses a viscosity below 100 mPas after two hours at 130°C, which indicates good stability and an extended process window at elevated temperatures. The press with the preform is heated up to 150°C in order to accelerate the infusion process by decreasing the viscosity of the uncured resin and additionally to ensure a good dissolution of **PI** within the liquid resin during the infusion. The right graph in Figure 7 shows that the viscosity of the resin at 150°C is below 100 mPas after 30 minutes. In this regard, it is observed that the G0939 fabric with dimensions of 65 cm X 35 cm X 2 mm is infiltrated with the resin system in less than one minute. Therefore, the applied preform temperature of 150°C is suitable for a fast infiltration of the resin system.

The T_g and the T_{onset} of the resulting **CE/PI/DABPA** CFRP laminates is 316°C and 280°C, respectively obtained by means of DMTA. The mechanical properties in terms of the ILSS value of the resulting material are illustrated in Figure 8.

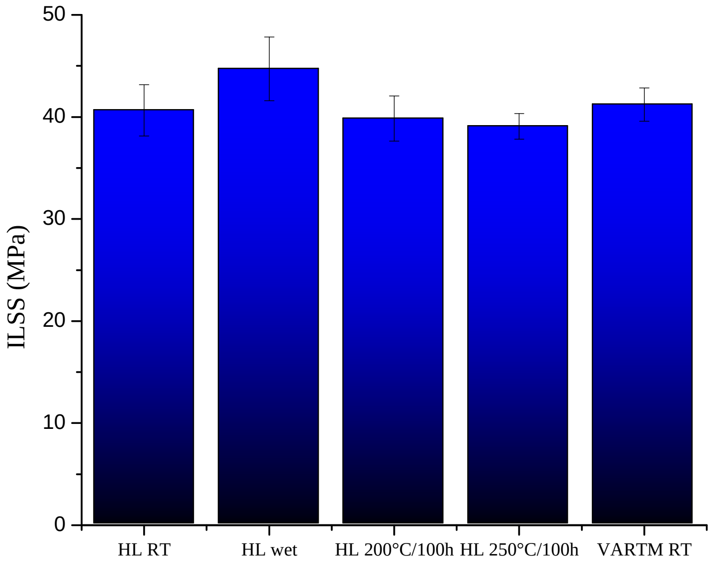

Figure 8: ILSS Values of **CE/PI/DABPA** (11 wt.-% **PI**) + G0939 CFRP laminates.

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Figure 8 shows that the ILSS value of the materials is ~43 MPa. The ILSS values of the material manufactured by VARTM shows less variation than the values of the handlaminated (HL) material. Most important, no decrease of the ILSS value can be observed after ageing of the material at 250°C over 100 h under oxidative conditions. In addition, the T_g and the T_{onset} of the thermooxidative aged material is 317°C and 269°C, respectively obtained by means of DMTA. In combination with the results from Figure 5, it can be concluded that no significant decrease of the thermo-mechanical properties can be observed up to 250°C.

4. Conclusions

The properties in terms of solubility, process stability, thermal as well as mechanical values of the recently developed resin system consisting of **CE**, **PI** and **DABPA** are determined. The uncured matrix is a homgenous liquid with a viscosity of 40 mPas at the infiltration temperature of 130°C. For the manufacturing of CFRP laminates, handlaminating as well as VARTM experiments are performed. It shows that with both processes, laminates with a good quality can be manufactured. With VARTM, a better laminate quality in terms of a higher fibre volume fraction and a consistant thickness can be obtained than with handlaminating. The results obtained by the ILSS experiments as well as the thermooxidative experiments reveal that no significant degradation of the material and consequently no decrease of the mechanical properties occur up to temperatures of 250°C over a longer period of time. Hence, the materials can be used for high temperature applications. In summary, the new material shows significantly decreased process parameters in terms of injection viscosity, injection temperature and curing temperature and beyond that reduced costs compared to commercial PETI resins.

5. Literature

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